CCL REPORT NO. 304

FINAL REPORT

ANALYTICAL METHOD FOR ETHYLENE DIBROMIDE DEPLETION IN AVIATION GASOLINE

BY

GEORGE G. ESPOSITO

MAY 1972

THIS DOCUMENT HAS BEEN APPROVED FOR PUBLIC RELEASE AND SALE; ITS DISTRIBUTION IS UNLIMITED

U. S. ARMY
ABERDEEN RESEARCH & DEVELOPMENT CENTER
COATING & CHEMICAL LABORATORY
Aberdeen Proving Ground
Maryland

9

ACCESSION for

NTIS White Section
DDC Buff Section
UNANNOUNCED
JUSTIFICATION..........

BY..........
DISTRIBUTION/AVAILABILITY CODES

Dist.	AVAIL. and/or SPECIAL
A	

DDC AVAILABILITY NOTICE

Qualified requesters may obtain copies of this report from Defense Documentation Center, Cameron Station, Alexandria, Virginia 22314

THE FINDINGS IN THIS REPORT ARE NOT TO BE CONSTRUED AS AN OFFICIAL DEPARTMENT OF THE ARMY POSITION, UNLESS SO DESIGNATED BY OTHER AUTHORIZED DOCUMENTS.

DESTROY THIS REPORT WHEN IT IS NO LONGER NEEDED. DO NOT RETURN IT TO THE ORIGINATOR.

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1 ORIGINATING ACTIVITY (Corporate author) U.S. Army Aberdeen Research & Development Center Coating & Chemical Laboratory Aberdeen Proving Ground, Md. 21005	2a REPORT SECURITY CLASSIFICATION Unclassified 2b GROUP

3 REPORT TITLE

ANALYTICAL METHOD FOR ETHYLENE DIBROMIDE DEPLETION IN AVIATION GASOLINE

4 DESCRIPTIVE NOTES (Type of report and inclusive dates)

Final Report

5 AUTHOR(S) (Last name, first name, initial)

Esposito, George G.

6. REPORT DATE	7a. TOTAL NO OF PAGES	7b NO OF REFS
May 1972	12	1

8a CONTRACT OR GRANT NO. AMCMS Code No. 502E.11.29500 b PROJECT NO. 1T062105A329 c d	9a ORIGINATOR'S REPORT NUMBER(S) CCL #304 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

10 AVAILABILITY/LIMITATION NOTICES

This document has been approved for public release and sale; its distribution is unlimited. Qualified requesters may obtain copies of this report from Defense Documentation Center.

11 SUPPLEMENTARY NOTES	12 SPONSORING MILITARY ACTIVITY
	U.S. Army Materiel Command Washington, D. C. 20315

13 ABSTRACT

The measurement of ethylene dibromide depletion in aviation gasoline is one criterion for evaluating the storage stability of coatings used for the corrosion prevention of tanks and containers used for the storage and protection of military petroleum based hydrocarbons fuels. The standard procedure for the determination of ethylene dibromide depletion is time-consuming, requires special equipment, and necessitates extraordinary care in handling. The method described in this report affords an accurate, uninvolved procedure for measuring ethylene dibromide depletion; the procedure is free from hazardous operating conditions and is highly reproducible.

DD FORM 1 JAN 64 1473

UNCLASSIFIED

Security Classification

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT

INSTRUCTIONS

1. ORIGINATING ACTIVITY: Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization *(corporate author)* issuing the report.

2a. REPORT SECURITY CLASSIFICATION: Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2b. GROUP: Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. REPORT TITLE: Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. DESCRIPTIVE NOTES: If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. AUTHOR(S): Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. REPORT DATE: Enter the date of the report as day, month, year; or month, year. If more than one date appears on the report, use date of publication.

7a. TOTAL NUMBER OF PAGES: The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. NUMBER OF REFERENCES: Enter the total number of references cited in the report.

8a. CONTRACT OR GRANT NUMBER: If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b, 8c, & 8d. PROJECT NUMBER: Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9a. ORIGINATOR'S REPORT NUMBER(S): Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. OTHER REPORT NUMBER(S): If the report has been assigned any other report numbers *(either by the originator or by the sponsor)*, also enter this number(s).

10. AVAILABILITY/LIMITATION NOTICES: Enter any limitations on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

(1) "Qualified requesters may obtain copies of this report from DDC."

(2) "Foreign announcement and dissemination of this report by DDC is not authorized."

(3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through ________________."

(4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through ________________."

(5) "All distribution of this report is controlled. Qualified DDC users shall request through ________________."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. SUPPLEMENTARY NOTES: Use for additional explanatory notes.

12. SPONSORING MILITARY ACTIVITY: Enter the name of the departmental project office or laboratory sponsoring *(paying for)* the research and development. Include address.

13. ABSTRACT: Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as *(TS)*, *(S)*, *(C)*, or *(U)*.

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.

Security Classification

UNCLASSIFIED

CCL REPORT NO. 304

FINAL REPORT

ANALYTICAL METHOD FOR ETHYLENE DIBROMIDE DEPLETION IN AVIATION GASOLINE

BY

GEORGE G. ESPOSITO

MAY 1972

AMCMS CODE NO. 502E.11.29500

DEPARTMENT OF THE ARMY PROJECT NO.

1T062105A329

U. S. ARMY
ABERDEEN RESEARCH AND DEVELOPMENT CENTER
COATING AND CHEMICAL LABORATORY
ABERDEEN PROVING GROUND
MARYLAND 21005

UNCLASSIFIED

ABSTRACT

The measurement of ethylene dibromide depletion in aviation gasoline is one criterion for evaluating the storage stability of coatings used for the corrosion prevention of tanks and containers used for the storage and protection of military petroleum based hydrocarbons fuels. The standard procedure for the determination of ethylene dibromide depletion is time-consuming, requires special equipment, and necessitates extraordinary care in handling. The method described in this report affords an accurate, uninvolved procedure for measuring ethylene dibromide depletion; the procedure is free from hazardous operating conditions and is highly reproducible.

TABLE OF CONTENTS

I. INTRODUCTION

Many fuel and water resisting protective coatings have been developed to maintain internal corrosion control of cargo tanks of barges, railway tank cars, tankers, trucks, surface and subsurface tanks. and tankers used for the bulk transportation and storage of a wide variety of military petroleum fuels. A number of different types of coatings have proved satisfactory for this service, and other coatings continue to evolve from research and development of new polymeric materials. A suitable fuel container coating must adequately protect tanks from corrosion, must not react with or contaminate the fuel, and must not be degraded by the environment.

Current military specifications prescribe requirements for the performance characteristics of coatings intended for lining the interior surfaces of fuel storage tanks. One of the tests used to determine the compatibility of protective coatings with hydrocarbon fuel is the ethylene dibromide depletion test. Ethylene dibromide is well known as an effective scavenger of lead deposits and at the present time, 3 - 4 gms/gallon are blended with aviation gasoline to offset the undesirable effects of antiknock organolead additives found in aviation gasoline. The test is conducted to determine if any reaction occurs between a coating material and ethylene dibromide in gasoline when they have had intimate contact over an extended period of time.

The bromine depletion test described in MIL-STD-1262 (Military Standard Degradation Tests for Fuels and Fuel Container Coatings) consists of exposing a coated test panel to aviation gasoline for 35 days and testing the exposed gasoline and control gasoline for bromine content. A sample of gasoline is added to sodium metal under cryogenic conditions followed by various treatments that are necessary for the decomposition of excess sodium and the elimination of interference from additives and impurities in the gasoline. Final measurement is accomplished by the potentiometric titration of bromides with silver nitrate solution. The procedure must be carefully monitored and extreme caution must be exercised to reduce the hazard of fire.

The procedure developed in this laboratory is based on the reaction described in Fieser and Fieser (1) for the formation of vinyl bromide.

$$BrCH_2CH_2Br \xrightarrow{\text{alcohlic KOH}} CH_2 = CHBr$$

Balancing the reaction gives,

$$BrCH_2CH_2Br + KOH \longrightarrow CH_2 = CHBr + KBr + H_2O$$

Since potassium bromide, one of the products, is easily determined by reaction with silver nitrate, conditions were established which favored the quantitative formation of potassium bromide. The proposed procedure is relatively easy to conduct and gives exceptionally good reproducibility.

A gasoline sample is refluxed with alcoholic KOH and potassium bromide is precipitated quantitatively from solution. The precipitate is washed free of gasoline, dissolved in water, and precipitated as the silver salt from an acid solution. The amount of ethylene bromide in the original sample is calculated from the weight of silver bromide.

II. DETAILS OF TEST

Reagents:

1. Alcoholic KOH, 1N.
   Dissolve 65 grams of potassium hydroxide in 1 liter of absolute ethanol. Filter immediately before using.

2. Silver nitrate solution, 5%.
   Dissolve 50 grams of reagent grade silver nitrate in 1 liter of distilled water.

Procedure:

Pipette 100 ml. samples of exposed and unexposed aviation gasoline into separate 250 ml. flasks with ground glass joints. Treat both samples in the following manner. Add 25 ml. of alcoholic KOH, attach an air condenser, and reflux for 2 hours in a 65 - 70°C. water bath (NOTE 1). Cool sample to room temperature and filter through a dry Gooch crucible containing a mat of asbestos, washing with benzene. Dry the flask and crucible at 100°C. Cool to room temperature and wash the contents of the flask through the crucible into a clean 500 ml. suction flask with about 100 ml. of distilled water. Quantitatively transfer the filtrate to a 400 ml. beaker, add 5 ml. of 7.5 N nitric acid, and dilute to 250 ml. with distilled water. While stirring, slowly add 10 ml. of 5% silver nitrate solution. Heat the solution to 80 - 90°C. and then cool to room temperature. Filter the sample through a tared Gooch crucible containing a mat of asbestos; quantitatively wash and transfer precipitate with 1% nitric acid; and finally wash until acid free with distilled water. Dry the crucible for 1 hour at 125 - 135°C., cool in dessicator, and weigh.

Calculation:

wt. of Br in 100 ml. gasoline = wt. of AgBr x 0.424

$$\text{grams ethylene dibromide/gallon gasoline} = \frac{\text{wt. of Br in 100 ml. gas.} \times 37.85}{0.8507}$$

NOTE 1: Use water bath in a well ventilated hood as the light ends of gasoline will distill from the sample through the air condenser.

III. RESULTS

Ethylene dibromide was quantitatively blended with unleaded gasoline to give known samples ranging from about 1 to 6 grams per gallon. The analytical results shown in Table I illustrate the high order of reproducibility of the method. Theoretical yields were obtained with samples A and B; however, yields were lower with the smaller samples, C and D. Low results can be improved by increasing the sample size as shown with Sample D. Moreover, ethylene dibromide depletion is generally determined on aviation gasoline containing levels of ethylene dibromide similar to Sample B.

Ethylene dibromide depletion was determined on several tank coating materials; the results are shown in Table II. Specifications usually allow up to 10% ethylene dibromide depletion.

IV. DISCUSSION

Larger samples would have improved the accuracy of the procedure with fuels containing very low levels of ethylene dibromide, but large sample would have produced some inherent problems, such as, longer time to reach reflux temperature, larger filtering volume, and increased volume of light ends being distilled into the hooded area.

During the early stages of procedure development, potassium bromide was extracted with water from the gasoline following the alkali treatment. This procedure gave consistently high results and further investigation showed that some of the additives and impurities, e.g., phenols and sulfides, formed insoluble silver salts which added to the weight of silver bromide. By filtering the solution after saponification, the insoluble potassium bromide was washed free of interfering materials and subsequent quantitative precipitation of silver bromide was made possible. The procedure can not be terminated by weighing the potassium bromide because of the presence of insoluble potassium carbonate salts that form during alkali treatment of the sample.

Leaded gasoline for automobiles may contain a chloride lead scavenger in addition to ethylene dibromide. When the procedure was applied directly to pure ethylene dichloride low results were obtained. Extending the reflux time and increasing the reflux temperature, greatly improved the yield for ethylene dichloride; but since a method of analysis for ethylene dichloride was not within the scope of the investigation the study was not pursued further. However, it is reasonable to believe that optimum conditions could be established for the analysis of both ethylene dibromide and ethylene dichloride.

V. REFERENCE

1. Fieser, L. F. and Fieser, M., Advanced Organic Chemistry, p. 340, Reinhold Corp., New York (1961).

APPENDIX A

TABLE I

Determination of Ethylene Dibromide in Aviation Gasoline

Sample	g/gallon Present	g/gallon Found	% Recovery
A	6.226	6.319; 6.230	100.7
B	3.113	3.092; 3.092	99.3
C	1.556	1.442; 1.442	92.7
D	0.933	0.773; 0.770	82.9
	0.933	0.877; 0.876	94.0*

*Used 200 ml. of sample.

TABLE II

Ethylene Dibromide Depletion

Sample	Ethylene Dibromide Depletion
A	0.5%
B	1.1
C	0.7